Relative Rate Studies of Chlorine Atoms with Crotonaldehyde and Methyl Vinyl Ketone

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Abstract

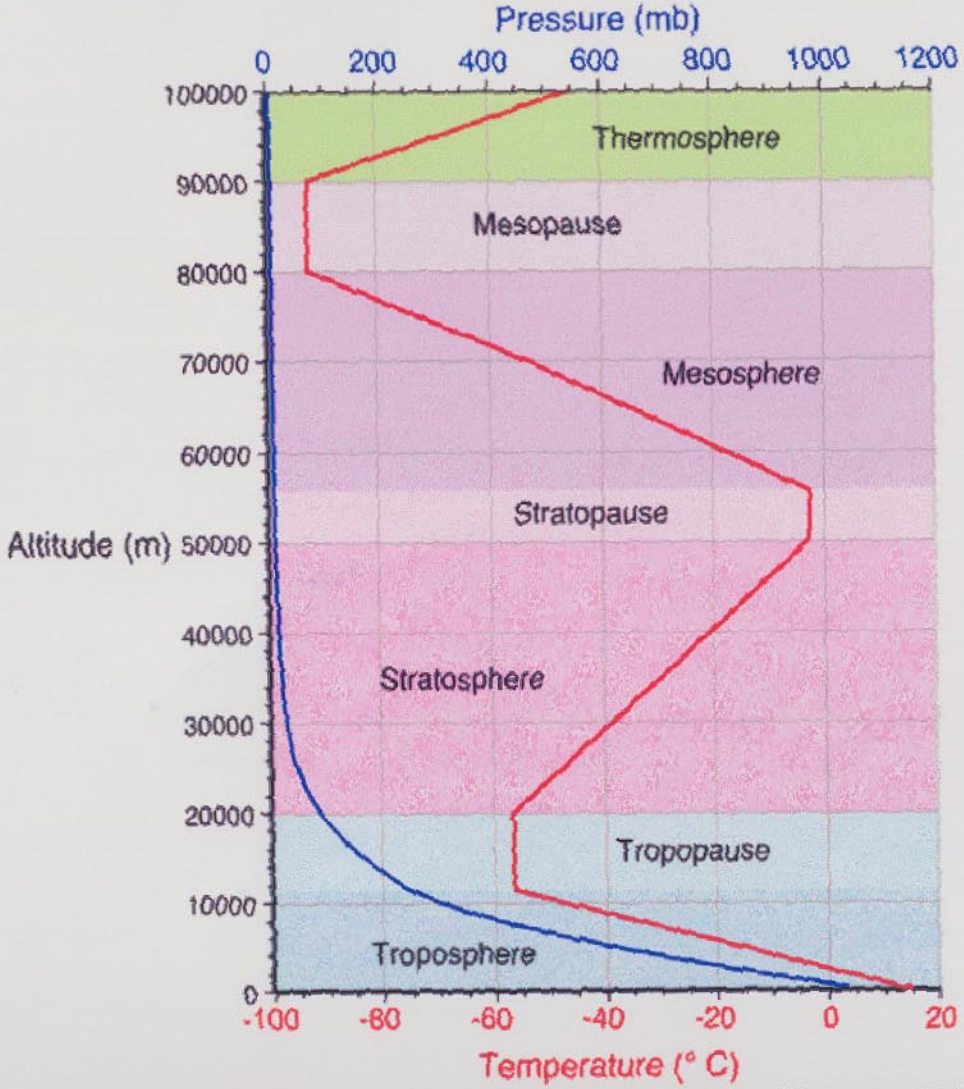
The relative rates of reactions of chlorine atoms (Cl) with two organic compounds, crotonaldehyde (CA) and methyl vinyl ketone (MVK), have been studied. Each organic compound along with Cl_2 was introduced into a 30 L Teflon bag with N_2 or air as diluent. The mixture was then photolyzed repetitively for brief periods and, after each photolysis cycle, a sample was analyzed using the analytical technique of gas chromatography-flame ionization detection (GC-FID). The rate constant for the reaction of MVK with Cl was determined to be $(2.3 \pm 0.5) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Preliminary data for the reaction of CA with Cl were obtained. These relative rates and their atmospheric implications are presented.

Motivation

- CCA and CMVK are considered unique chlorine-containing compounds that can serve as "markers" of chlorine atom chemistry.

- Wang and Finlayson-Pitts (2001) identified CCA and CMVK as the chlorine-containing products from the chlorine atom reaction with the anthropogenic specie 1,3-butadiene.

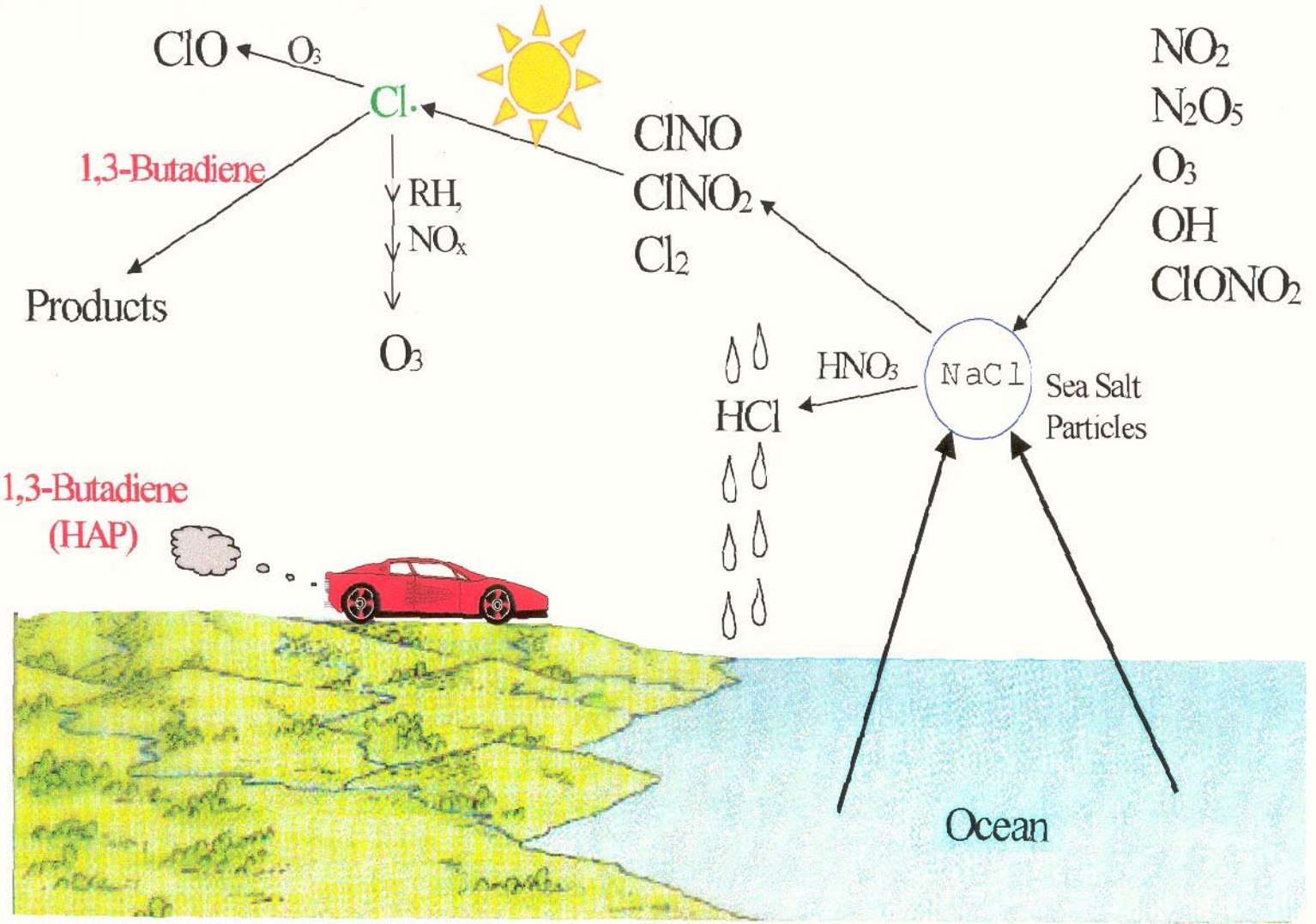
Atmospheric Layers



- Variations are due to alterations in the chemical and physical nature of the atmosphere with altitude.
- Troposphere contains about 75% of the total mass of the atmosphere.
- Stratosphere is also called the ozone layer.

Created by M. J. Pidwirny, Department of Geography, Okanagan University College

Cl Chemistry in Coastal Areas



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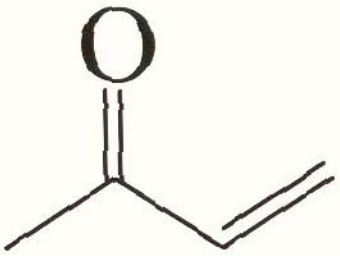
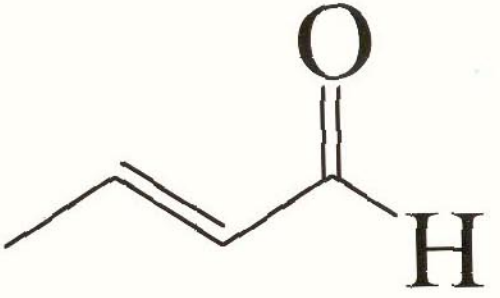
Reactions of Cl•

- Generation of Cl radical from salt
  - $NaCl + 2NO_2 \rightarrow NaNO_3 + ClNO$
    - Photolysis: $ClNO + h\nu \rightarrow NO + Cl\bullet$
  - $NaCl + N_2O_5 \rightarrow NaNO_3 + ClNO_2$
    - Photolysis: $ClNO_2 + h\nu \rightarrow NO_2 + Cl\bullet$
- Reactions with organics
  - Abstraction
    - $RH + Cl\bullet \rightarrow HCl + R\bullet$
  - Addition
    - $R_2C{=}CR_2 \rightarrow R_2C^{\bullet}\text{-}CR_2Cl$

Studied Compounds



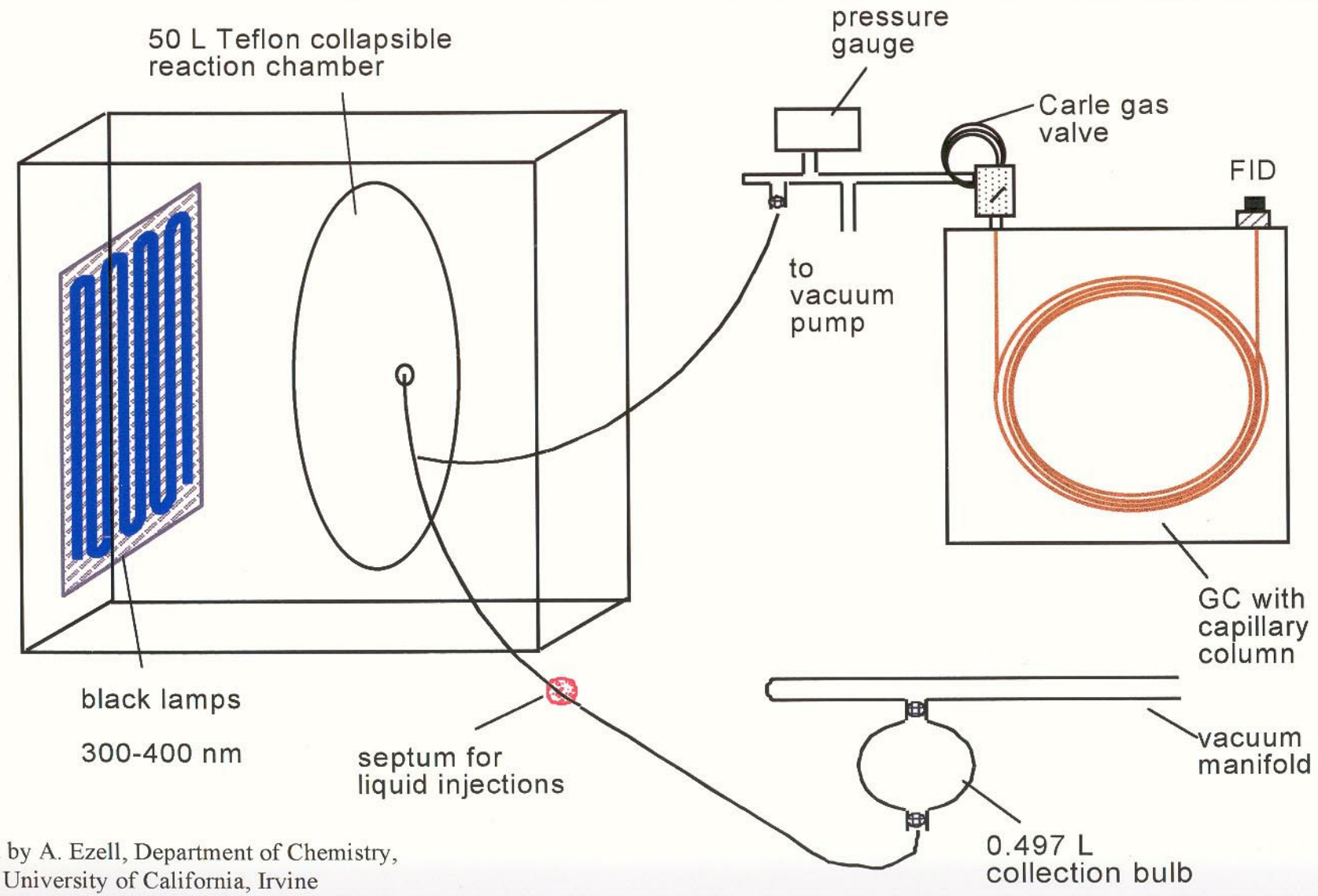
Methyl Vinyl Ketone



Crotonaldehyde

Nonane

Experimental Apparatus



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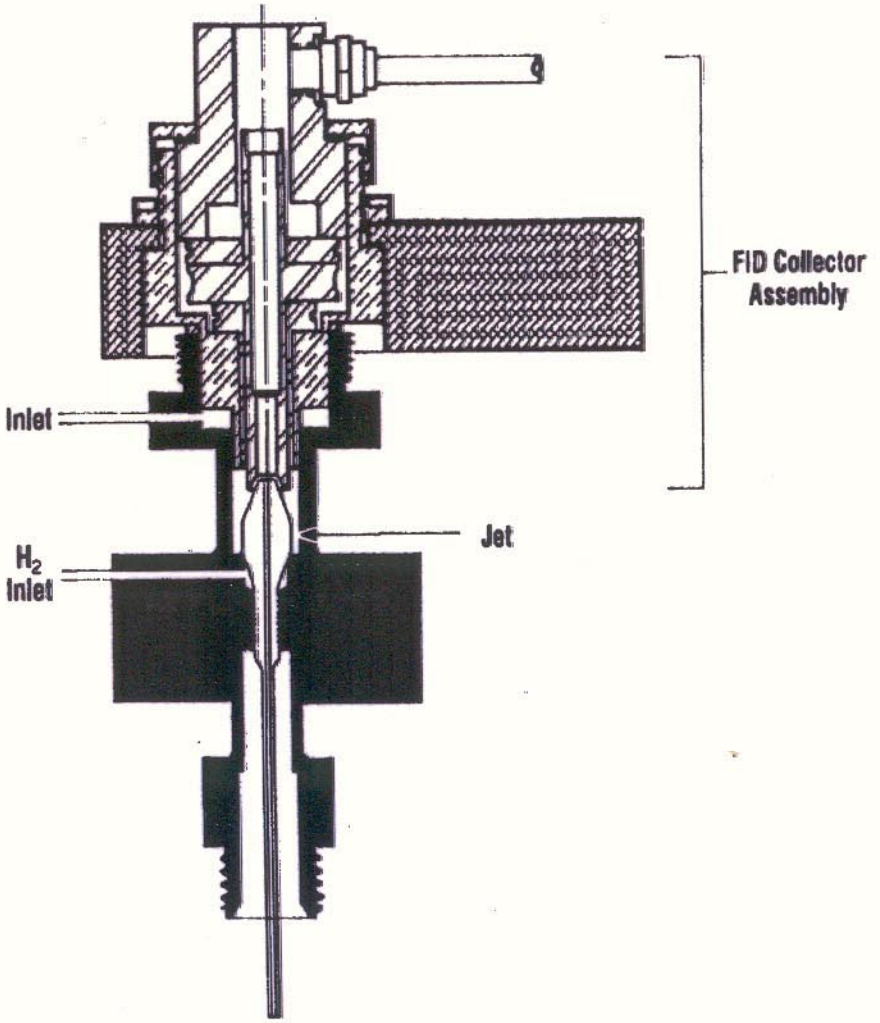
University of California, Irvine

Flame Ionization Detector (FID)



From HP 5890 SERIES II Gas Chromatograph Reference Manual

- Most used detector for gas chromatography.
- Responds to compounds that produce ions and electrons when burned in a H_2-air flame.
- Insensitive toward non-combustible gases.

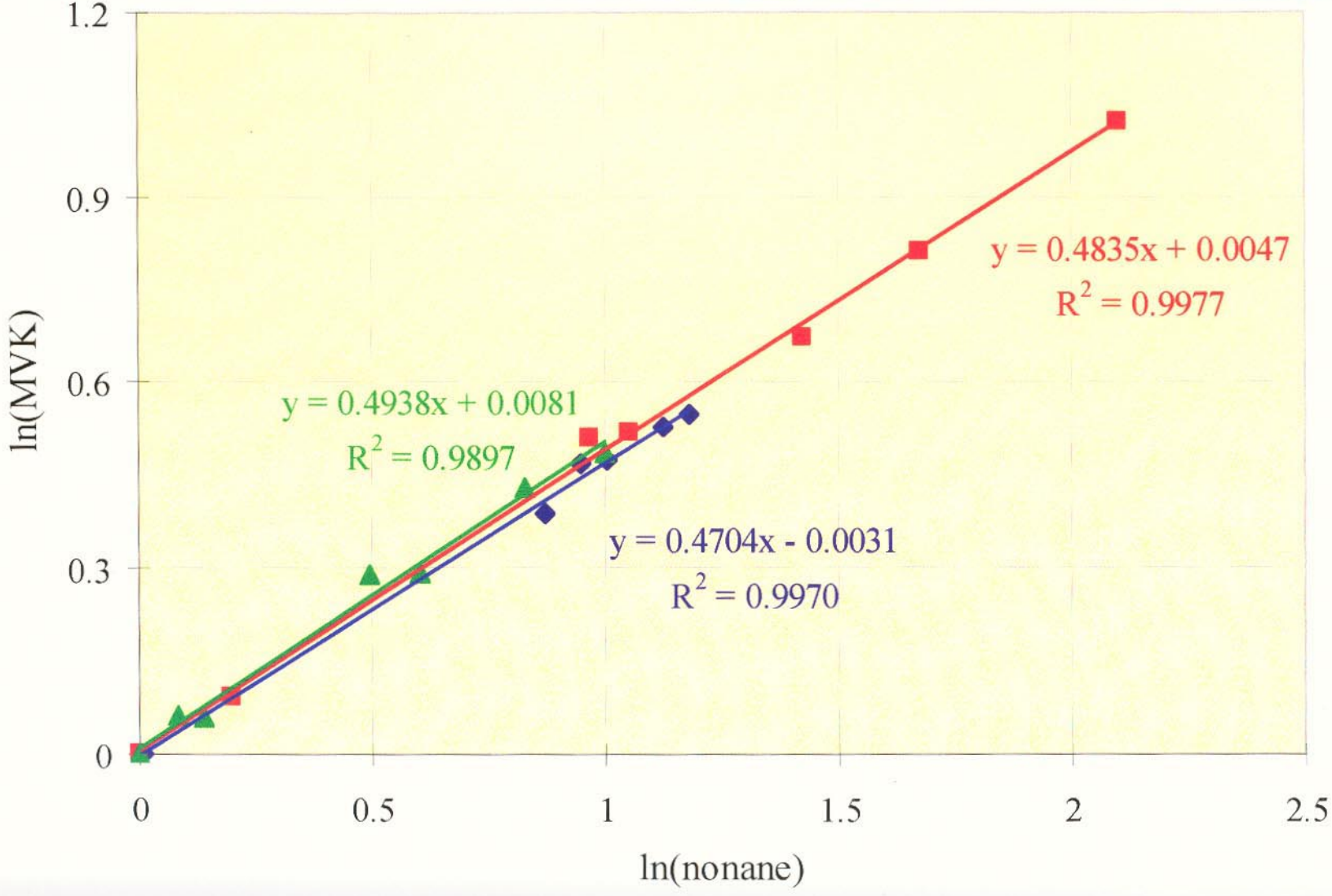
Relative Rate Technique

- Reference compound
  - Nonane
- Organics of interest
  - MVK
  - CA
- Ratio of rate constants
  - $$\ln\left(\frac{[\text{organic}]_0}{[\text{organic}]_t}\right) = \left(\frac{k_{\text{organic}}}{k_{\text{ref}}}\right) \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right)$$

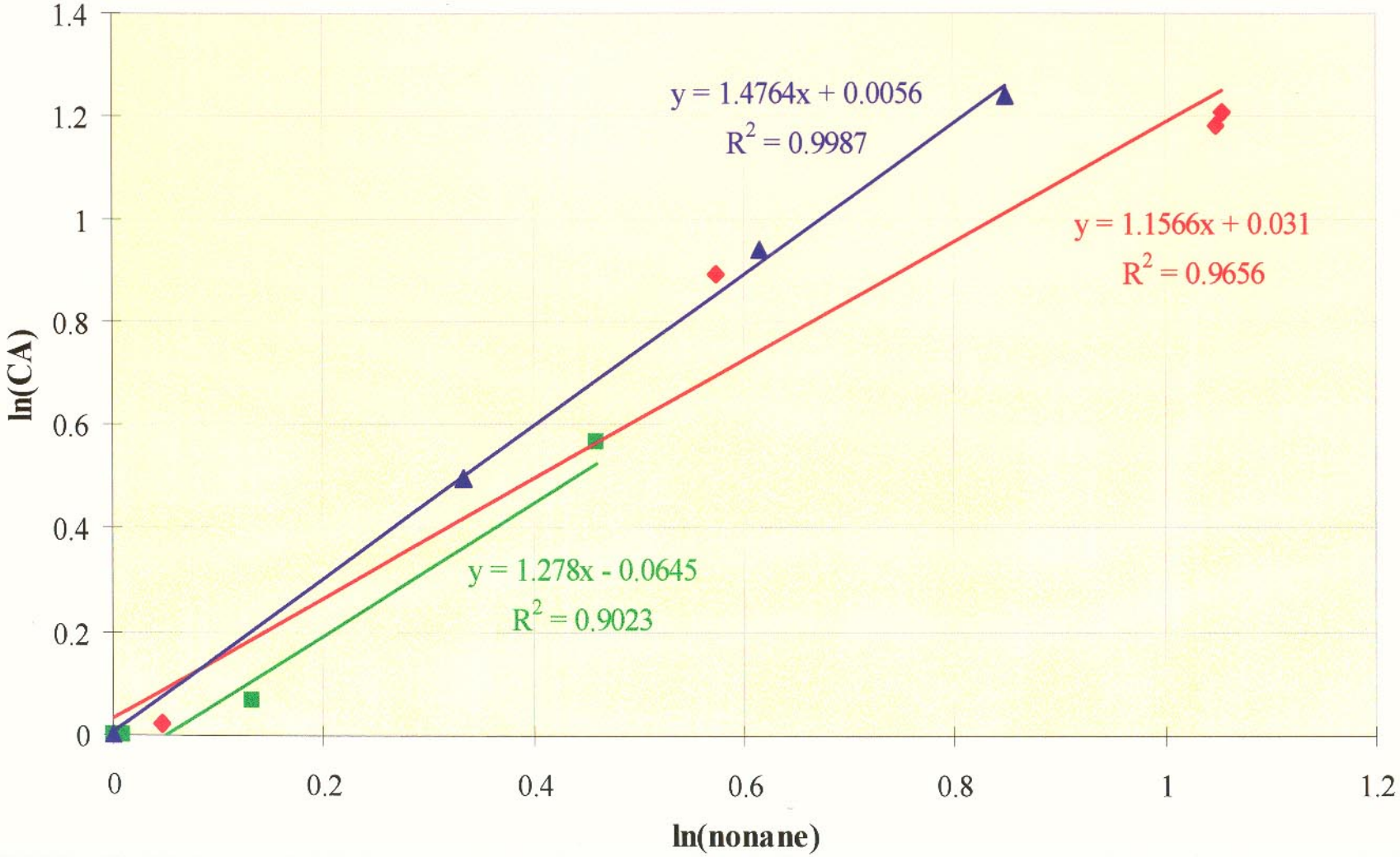
Relative Rates Methodology

- Sampling
  - Prepare mixtures of reference, organic and chlorine.
- Data Collection
  - GC-FID measures the loss of organic compounds after photolysis.
- Data Analysis
  - $$\ln\left(\frac{[\text{organic}]_0}{[\text{organic}]_t}\right) = \left(\frac{k_{\text{organic}}}{k_{\text{ref}}}\right) \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right)$$

Relative Rates of Methyl Vinyl Ketone *versus* Nonane



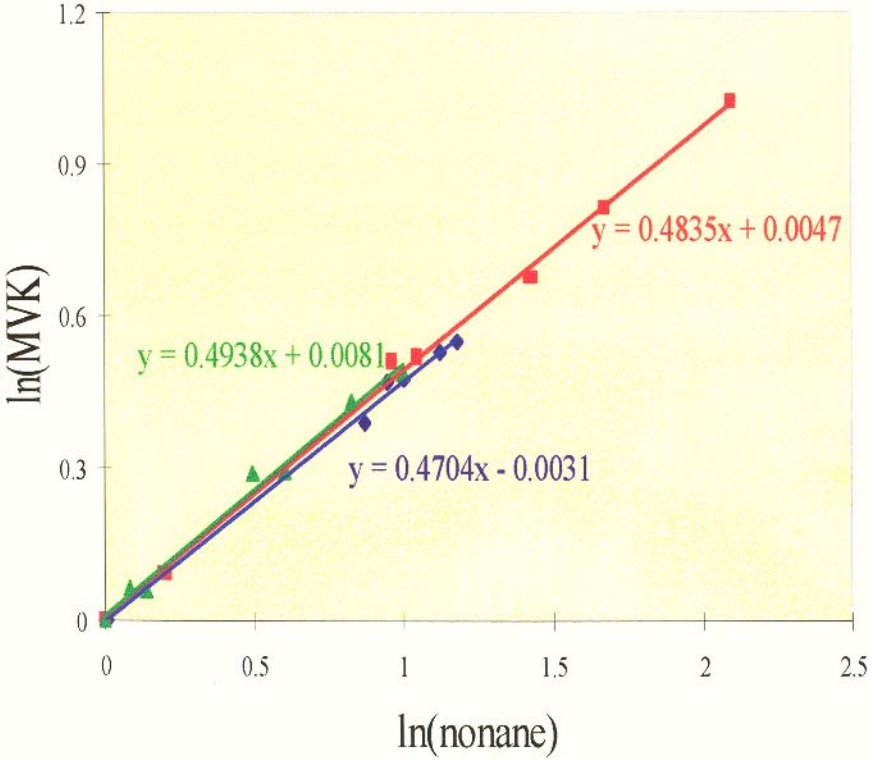
Relative Rates of Crotonaldehyde *versus* Nonane



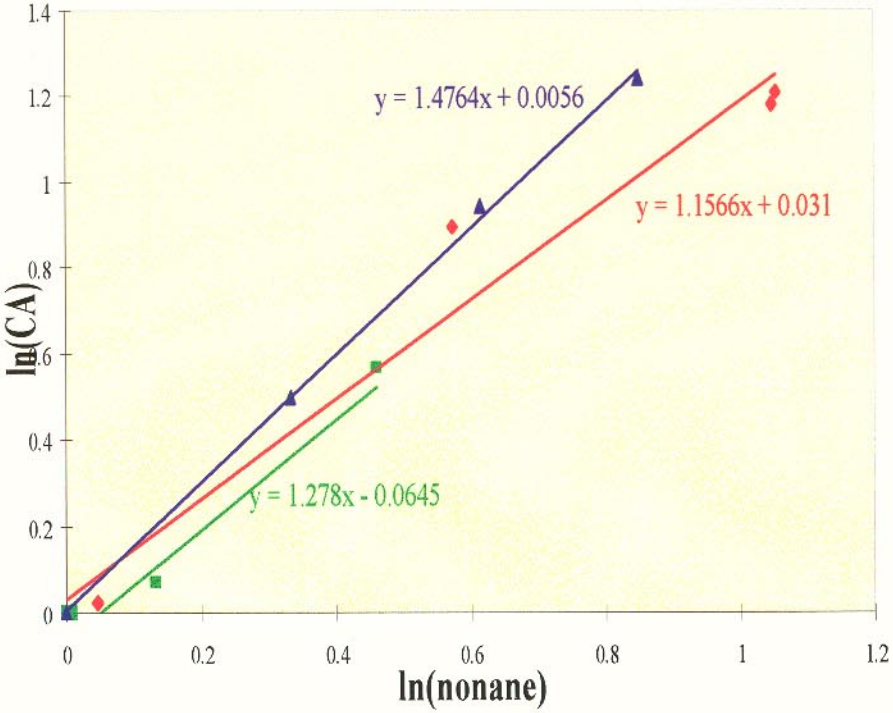
Results of Relative Rates

Organic Compound	k_{ref} (10^{-10} cm^3 $molecule^{-1}$ s^{-1})	Relative Rate $k_{organic}/k_{ref}$	$k_{organic}$ (10^{-10} cm^3 $molecule^{-1}$ s^{-1})
MVK	4.8	0.49 ± 0.11	2.3 ± 0.5
CA	4.8	1.3 ± 0.5	6.0 ± 2.4

Experimental Results



MVK *vs* Nonane



CA *vs* Nonane

Conclusions

- The rate constant for the reaction of MVK with Cl was determined to be $(2.3 \pm 0.5) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.
- The rate constant for the reaction of CA with Cl was determined to be $(6.0 \pm 2.4) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.
- The rate constant for CA seems to be high and hence not reasonable, thus more experiments need to be done regarding this reaction.

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